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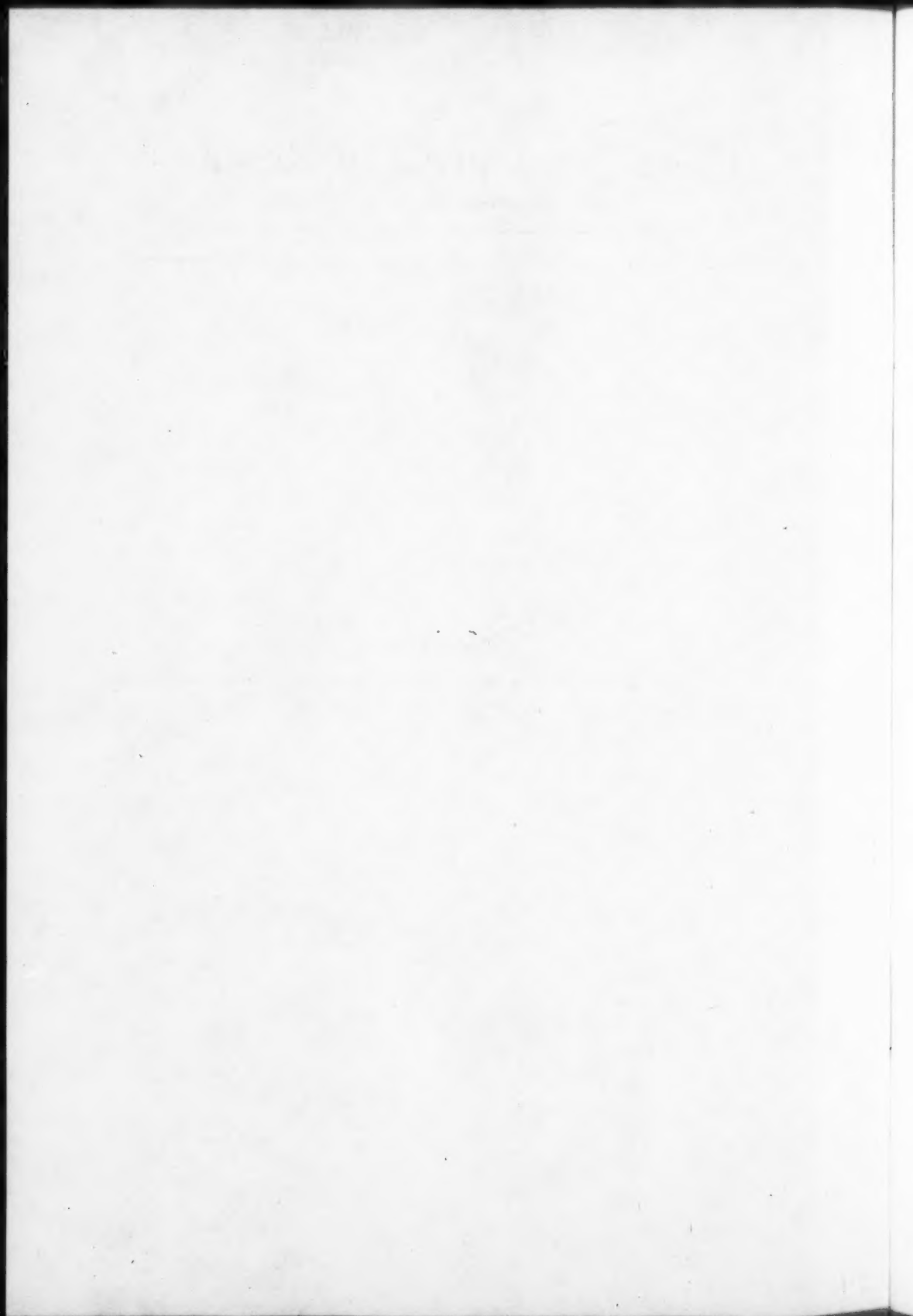
EDITOR'S NOTE

Material scheduled for publication in this issue will appear later.
This title page is included for purposes of record.

SELENIUM IN SOILS, GRAINS, AND PLANTS IN ALBERTA[1]

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Abstract

Two hundred and twenty-seven samples of wheat, forty soils, and four plants of the *Astragalus* family, all from the province of Alberta, have been analysed for their selenium content. The selenium content of the soils varied from less than 0.1 to 1 p.p.m., that of wheat, from less than 0.1 to 1 p.p.m., and that of *Astragalus* plants, from 0.3 p.p.m. in the root of one plant to 600 p.p.m. in the stalks of another. The majority of the wheat samples contained only traces of selenium, and in no case can any one be considered as dangerous. Some of the soils contained over 0.5 p.p.m. of selenium and these may be looked upon as seleniferous. Not enough data are available to indicate the extensiveness of seleniferous soils. Although the underlying strata of much of Alberta is of Upper Cretaceous Age, the soil is derived mostly from glacial drift formed from other types of rock, so that the seleniferous area may be much smaller than that earlier suspected. Analyses of wheat and soils indicate that dangerous areas are more likely to be found in southern Alberta than in central Alberta. Analyses of vetches show that the amount of selenium absorbed is independent of the species and the selenium content of the soil and varies with the part of the plant examined.

In recent years a great deal of attention has been paid to elements occurring in small amounts in water, soils, rocks, and plants, especially from the standpoint of their effect on humans and animals. Selenium is one that has been found to be harmful, as Beath and his coworkers in Wyoming (17, p. 14) and Franke and his coworkers (7, 8) in South Dakota have shown that "alkali disease" and "blind staggers" are caused by selenium in the diet. The toxicity of this element depends on the form in which it is ingested, in the following order: wheat >corn >barley >selenate >selenite (6). In plants, the selenium is present in the protein fraction and it has been shown that the toxic fraction is concentrated when a separation of proteins from other material is carried out. In foodstuffs, a selenium content of about 4 p.p.m. prevents normal growth.

Selenium in plants is derived from the soils in which they grow, but there seems to be no relation between the selenium content of the soils and that of the plants. Plants may be divided into three classes depending on their tolerance for selenium (9); (*a*) those that absorb large amounts of selenium

even from inorganic material, (*b*) those that absorb moderate amounts, (*c*) hose that have a limited tolerance for the element and are either absent from, or grow very poorly in, soils containing much selenium.

Examples of plants of the first type are certain of the vetches of the *Astragalus* family.   Cereals fall into the second class and some of the grasses as well as many other native plants fall into the third group.   The vetches grow vigorously on seleniferous soils and may contain many times more selenium than the soils on which they grow.   These may be and are used as "indicator" plants (15) for locating the presence of selenium in the soil.   It is believed that these are the only plants that can utilize the selenium from such inorganic substances as selenides, selenites, and selenates.   The selenium is stored in these plants in proteins which contain the selenium tied up in the same manner as sulphur in the commoner proteins.   When these plants decay, the selenium is returned to the soil in the form of organic selenium (1). Cereals and other plants of the second class do not utilize inorganic selenium but grow fairly well on seleniferous soils and absorb moderate amounts of selenium if the element is present in organic compounds generally formed from the decay of "indicator" plants.   Plants of the third group seem to have their growth retarded by selenium in the soil.

The consensus of opinion at the present time is that soils containing 0.5 p.p.m. of selenium or more should be suspected of being producers of toxic crops (10).   It has also been found that the tendency of plants to absorb selenium is decreased if the rainfall is more than 21 in.

All soils contain some selenium but those derived from rocks of the Upper Cretaceous Period generally contain larger amounts than those derived from rocks of other Periods, so that the crops grown on such soils are more likely to be toxic than those grown on soils from other sources.   Rocks of this Period extend from the Prairie Provinces down to the Gulf of Mexico, east of the Rocky Mountains, and there is a possibility that vegetation grown in soils derived from them will contain quantities of selenium.   In such states as Wyoming, South Dakota, North Dakota, and Montana the more out-standing seleniferous soils are on the Pierre and Niobrara formations of the Upper Cretaceous system, the former of which correspond in age to the Belly River series and the Bearpaw series of Alberta and Saskatchewan.   Since in the neighbouring states of Montana and North Dakota selenium poisoning is endemic, it would naturally be expected that similar conditions would prevail in the Prairie Provinces, because of the selenium in the soils and in the plants grown on these soils.   The first positive proof of this was found by Robinson (12) who noted the presence of 1.9 p.p.m. of selenium in a sample of Saskatchewan wheat.

Since wheat is one of the main crops of the Prairie Provinces it would seem to be logical to examine this cereal as well as soils in order to determine whether any district produces wheat of high enough selenium content to render it toxic and thus dangerous for human consumption.   Three studies of this nature were begun in 1938, by Byers of the U. S. Department of

Agriculture (4, 16), by Thorvaldson of the University of Saskatchewan (14), and by the writers at the University of Alberta. The present project had been under way for nearly a year before it was known that other investigators were interested in the selenium problem in Canada.

Byers' reports indicate the presence of large areas of seleniferous soils in Alberta, Saskatchewan, and Manitoba, with selenium content from 0.1 to 6 p.p.m., and vegetation, chiefly from the *Astragalus* family, with selenium content from 3 to 4190 p.p.m. His soils were mostly those in which "indicator" plants were growing. Thorvaldson examined 230 composite wheat samples and found an average selenium content of only 0.44 p.p.m., with a maximum of 1.5 p.p.m.

The present investigation was carried out primarily on samples of wheat. The examination was restricted to the ripened seeds even though it is known that the stem and the leaf may contain more selenium. A number of soils also were examined as well as some plants of different species of *Astragalus*, namely, *A. bisulcatus* and *A. pectinatus*. Samples of wheat of the 1938 crop were supplied by the Department of Field Crops of the University and by several mills at Medicine Hat. Many of the soils were collected from garden plots in 1935 by graduates of the University; the remainder, along with selenium bearing plants growing thereon, were gathered in 1939 by the Alberta Soil Survey unit of the Dominion Department of Agriculture.

The samples were so selected that a fair distribution from different parts of the province was obtained, with considerable emphasis placed on the southern half of the province, where outcrops of shales of Belly River and Bearpaw formations are more frequent.

Many methods for determining selenium in small quantities were examined critically, and for wheat and soils the one chosen was that of Robinson, Dudley, Williams, and Byers (13) with the modifications suggested by Curl and Osborn (5). In this procedure large amounts of hydrobromic acid are used, so it was found necessary to recover this by distillation as the constant boiling acid. Some of the waxy material from the wheat distilled over with the hydrobromic acid, giving a cloudy liquid with which it was difficult to obtain a satisfactory value for selenium. Satisfactory results were obtained by adding one-tenth of one per cent by weight of fresh bentonite to the hydrobromic acid filtrates, allowing to stand overnight, and then filtering. Fractional distillation was then carried out. The first third of the constant boiling acid was decolorized with sulphur dioxide, allowed to stand overnight, and filtered. It was then ready for use once more.

The weight of sample of wheat or soil used was 10 gm. although some determinations were carried out with 30-gm. samples. Weights were based on air dried material. Grains were ground up in a mill, and soils were ground in a mortar.

Two hundred and twenty-seven (227) samples of wheat were analysed. The results are summarized in Table I. Two hundred and six (206) of these

TABLE I

SELENIUM CONTENT OF WHEAT SAMPLE

Se, p.p.m.	Number of samples	Se, p.p.m.	Number of samples
<0.1	110	0.5	7
0.1	50	0.6	5
0.2	21	0.7	2
0.3	17	0.9	2
0.4	10	1.0	3

samples were grown in soil over Upper Cretaceous rocks, ninety-seven (97) over Belly River, and thirty-six (36) over the Bearpaw series. The classification of rocks used in this paper is taken from the geological map of Alberta published by Dr. J. A. Allan in 1937 under the auspices of the Research Council of Alberta. The underlying rocks may be of little significance in this province as they are covered in most places by layers of glacial drift differing greatly in thickness, so that only in a few places are beds covered by soils formed directly from rock strata below. It would be supposed that erosion would lower the selenium content of glacial drift by removal of soluble selenium compounds by washing them away. Then again the glacial drift may have been formed to a great extent from rocks that are not seleniferous. This may account for the lack of absorption of selenium as shown by the bulk of the wheat samples examined. As 4 p.p.m. of selenium is looked upon as the minimum amount of the element that is toxic in foods, it can be seen that the selenium content of the wheat examined is well below the toxic level.

Similar results were obtained in the examination of the soils. Twenty-seven of these soils, which had not been collected from the same plots as the samples of wheat, were stored in glass stoppered bottles from 1935 to 1938. These were so chosen as to represent a cross-section of the province. Thirteen were collected in 1939 and were taken from spots from which the *Astragalus* plants were obtained. Table II contains the results of analysis of the first series of soils. The results for the remaining 13 soils are shown with those for the selenium collecting plants in Table III.

If we look upon a soil containing 0.5 p.p.m. of selenium as dangerous, it can be seen that six of these fall in this category. These high selenium soils were taken at Coutts, Nemiscam, and Medicine Hat in the southern part of the province and at Blackfalds, Delburne, and Raven in the central part. Soils with low values for selenium were widely distributed over the southern and central parts of the province. These results compare favourably with those of Byers (16) whose values for soils from Alberta vary from 0.1 to 1.5 p.p.m. of selenium. It must be remembered, however, that all his samples came from southern Alberta and were chosen mostly because of the proximity of "indicator" plants.

TABLE II
SELENIUM CONTENT OF ALBERTA SOILS

Se, p.p.m.	Number of samples	Se, p.p.m.	Number of samples	Se, p.p.m.	Number of samples
<0.1	16	0.3	1	0.8	1
0.1	1	0.4	1	0.9	2
0.2	2	0.7	2	1.0	1

TABLE III
ANALYSIS OF SOILS AND PLANTS

Sample		Location	Geological formation	Se, p.p.m.
Soil	0-12 in.	12-5-6-W4	Belly River	0.5
"	12-24	"	"	0.4
"	24-36	"	"	0.4
"	36-48	"	"	0.4
A. bisulcatus	Roots	"		0.3
"	Stalks	"		3.0
"	Leaves	"		5.0
Soil	0-12 in.	34-6-5-W4	Bear Paw	0.3
"	12-24	"	"	0.4
"	24-36	"	"	0.3
"	36-48	"	"	0.5
A. bisulcatus	Roots	"		360
"	Stalks	"		465
"	Leaves *	"		170
Soil	0-12 in.	10-2-4-W4	Bear Paw	0.7
"	12-24	"	"	0.3
"	24-36	"	"	0.3
"	36-48	"	"	0.4
A. pectinatus	Stalks	"		30
"	Leaves	"		120
A. bisulcatus	Roots	"		220
"	Stalks	"		200
"	Leaves	"		600
Soil	0-12 in.	20 ft. from previous	Bear Paw	0.4

** This sample contained some soil that could not be separated. This may explain the low
selenium content for these leaves.*

Astragalus plants, along with the soils in which they grew, were collected
in late July, 1939, from the southeastern corner of the province on and near
the Dominion Range Experimental Station at Manyberries. The plants
were about a week beyond the blossoming stage. The soils come from both
the Belly River and the Bearpaw formations and samples were taken at
various depths. The plants were air dried and separated roughly into roots,
stalks, and leaves. Table III contains the results of the analysis of these
portions of the plants and the corresponding soils. Plants of this family
collected by Byers (16) in Alberta varied in selenium content from 12 to
3690 p.p.m.

Even though the maximum amount of 0.7 p.p.m. of selenium was found in these samples of soil, the vegetation grown on them was quite seleniferous. There is no relation between the selenium content of the plant and that of the soil. It will be noticed that plants of the same species grown on soils of similar selenium content differ greatly in the amount of selenium absorbed. It will also be noted that the selenium content of the plants generally increases from the root, to the stalk, and to the leaves. The results shown here correspond to those found by Byers (2, 3, 4, 15, 16), by Painter (11), and other workers.

The results presented in this paper must be regarded as preliminary in character. Sufficient evidence has been collected to indicate that there are areas in the province of Alberta where the soil contains sufficient selenium to render certain plants dangerous to the health of man and animals. From the examination of wheat it would seem that the selenium content is sufficiently low that the possibility of harmful effects from this source is very remote. No work has yet been done on vegetables, hay, grass, or other forage crops. The whole matter of possible selenium poisoning in Alberta can be cleared up only by an intensive survey of the area from the standpoint of selenium content of soils and all types of vegetation.

Acknowledgment

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CONTRIBUTION TO THE STUDY OF THE PRECIPITATION OF CARBONATES, BORATES, SILICATES AND ARSENATES[1]

By Paul E. Gagnon[2], Louis Cloutier[2] and R. Martineau[3]

Abstract

A study was made of the precipitation, at room temperature, of the carbonates of cadmium, cobalt, and nickel, of the chromate of beryllium, of the borates of zinc, of the silicates of copper and of the arsenates of lead. A rapid-mixing apparatus that insured that the precipitations took place in homogeneous liquid medium was used. In each series of experiments, the concentration of one reacting solution was kept constant and that of the other systematically varied. The values of the molar ratio of oxides, CdO/CO_2 for example, in the precipitates were found by analysis. If they remained constant with different concentrations of reactants, a definite compound was indicated. The normal cadmium carbonate was obtained. Three definite basic compounds, not described in the literature, were prepared: a definite basic carbonate of cobalt, $5CoCO_3.Co(OH)_2$, and two definite basic arsenates of lead, $4Pb_3(AsO_4)_2.Pb(OH)_2$ and $9Pb_3(AsO_4)_2.Pb(OH)_2$. Dilead arsenate, $PbHAsO_4$, was easily precipitated, but trilead arsenate, $Pb_3(AsO_4)_2$, only under very specific conditions. The other precipitates were all mixtures. The influence of the hydrogen ion concentration of the solutions on the composition of the precipitates formed was determined.

Introduction

The composition of precipitates obtained by mixing solutions often varies not only according to the concentration of the reagents and to the temperature but also according to the method of precipitation. The last factor is much more important than it was at first believed to be. This explains why so many authors have obtained different results although using the same solutions. In the case of solutions apt to form basic salts, a whole series of mixtures may be obtained, their composition ranging from that of the hydroxide to that of the normal salt. These mixtures have often been assumed to be definite compounds. Consequently, when the study of a precipitation is planned, the method of mixing the solutions must be taken into account so that the precipitates be formed in homogeneous medium.

To realize a rapid mixing of two solutions and obtain homogeneous precipitates, Pierre Jolibois has designed an apparatus and proposed a procedure that has been followed for the study of numerous precipitations (2, 3, 7, 8, 9, 10, 12).

The main object of this work was to apply Jolibois' method to the study of the precipitation, at room temperature, of the carbonates of cadmium, cobalt and nickel, of the chromate of beryllium, of the borates of zinc, of the silicates of copper and of the arsenates of lead.

Procedure

Since a detailed description of the apparatus used can easily be found in the literature (3, 7, 12), it is not necessary to repeat it here.

The present authors generally used only two reactants, e.g., four litres of a solution of cadmium nitrate, $M/20$, was mixed very rapidly with four litres of a solution of potassium acid carbonate, $M/20$. The precipitate formed was filtered off and analysed. The experiment was repeated with four litres of solutions of cadmium nitrate of the same concentration, $M/20$, and four litres of solutions of potassium acid carbonate of different concentrations ranging from $M/20$ to $M/2$. The values of the molar ratio of oxides CdO/CO_2 found for the precipitates were tabulated and plotted against the corresponding values of the molar ratio of oxides CO_2/CdO in the solutions.

Whenever the value of the molar ratio of oxides in the precipitates remained constant for successive increasing values of the molar ratio of oxides in the solutions, a definite compound was indicated, whereas, if the composition of the precipitates varied, a mixture had been obtained.

General Results

The reactions of solutions of cadmium nitrate with solutions of potassium acid carbonate always yielded the normal carbonate of cadmium, whereas with solutions of ammonium carbonate more basic precipitates were obtained.

The precipitation of solutions of cobalt nitrate by those of potassium acid carbonate gave a definite basic compound, $5CoCO_3 \cdot Co(OH)_2$, which has not been described in the literature, whereas solutions of ammonium carbonate gave unstable products that decomposed with loss of carbon dioxide.

When solutions of nickel nitrate and of ammonium carbonate were used, basic mixtures were first formed, but, when the value of the molar ratio CO_2/NiO in the solutions was higher than 7.0, the nickel remained in solution as nikelo-ammonic cations. Potassium acid carbonate did not give precipitates in sufficient quantity to be studied.

The hydrogen ion concentration has a marked influence on the composition of the carbonates obtained by precipitation. The influence of the carbonate ions is lessened by the concentration of the hydrogen ions.

The beryllium carbonates decomposed immediately after their formation by giving off carbon dioxide, and the beryllium chromate was hydrolysed by washing. Hence, it was impossible to study these compounds.

The precipitates prepared from solutions of zinc nitrate and solutions of borax, or of borax and sodium hydroxide, were all basic mixtures.

Solutions of copper sulphate treated with those of sodium metasilicate gave basic or acid mixtures, and, when treated with solutions of sodium metasilicate and sodium hydroxide, yielded only basic mixtures.

When solutions of lead nitrate reacted with those of arsenic acid or of monopotassium arsenate, dilead arsenate was always precipitated. However,

when there was an excess of arsenate ions, the precipitates adsorbed some and were not pure.

The reaction between solutions of lead acetate and of arsenic acid gave the same results, although, in this case, a slight excess of arsenic ion had no influence on the purity of the precipitates.

Solutions of lead chloride gave by reaction with arsenic acid indefinite lead chloroarsenates.

Solutions of lead nitrate and of dipotassium arsenate produced, depending on the concentration, dilead arsenate, $PbHAsO_4$, trilead arsenate, $Pb_3(AsO_4)_2$, and the definite basic arsenate $9Pb_3(AsO_4)_2 . Pb(OH)_2$. The first two are well known, whereas the last has not yet been mentioned in the literature.

Solutions of lead nitrate treated with those of arsenic acid and potassium hydroxide gave basic mixtures. However, with very dilute solutions of potassium hydroxide, dilead arsenate was obtained.

Finally, solutions of lead nitrate and of arsenic acid containing ammonium hydroxide yielded dilead arsenate and a definite basic arsenate $4Pb_3(AsO_4)_2 . Pb(OH)_2$, which has not yet been described.

None of the basic arsenates of lead mentioned in the literature could be obtained by the present authors under the conditions maintained.

The composition of the arsenates that were prepared did not change when stirred for 24 hr. with their mother liquors.

The pH values of all the mother liquors of the arsenates were determined and the influence of the hydrogen ion concentration on the composition of the precipitates was ascertained.

Experimental and Results

CADMIUM CARBONATES

Schulten (18) obtained crystals of the normal carbonate by washing with aqueous ammonia the precipitate obtained by adding an excess of ammonium carbonate to a concentrated solution of cadmium chloride and heating the diluted mixture on a water-bath.

The present authors, using solutions of cadmium nitrate, $M/20$, and of potassium acid carbonate of different concentrations, $M/20$ to $M/2$, always obtained the normal carbonate of cadmium. With solutions of cadmium nitrate, $M/20$, and of ammonium carbonate of different concentrations, $M/20$ to $M/2$, precipitates slightly more basic than the normal cadmium carbonate were obtained.

Since other authors (3) obtained two definite basic carbonates but no normal carbonate of cadmium by interaction of solutions of cadmium nitrate $M/20$, and of normal potassium carbonate, $M/40$ to $3/4$ M, instead of solutions of potassium acid carbonate or ammonium carbonate, it may be concluded that the composition of the cadmium carbonate formed by precipitation is greatly influenced by the hydrogen ion concentration.

Before being analysed, the precipitates were filtered off, washed thoroughly with cold distilled water, and dried at 80° C. Qualitative tests indicated that the precipitates were free from potassium or ammonium ions. Since the carbonates still contained water, the carbon dioxide and the metal were determined on the same portion of the sample. Carbon dioxide liberated by hydrochloric acid (1 : 1) was absorbed in weighed soda-lime tubes and the resulting cadmium chloride solution was treated with concentrated sulphuric acid and evaporated to dryness on the steam-bath. The residue was dissolved in water and the solution brought up to 250 cc. in a graduated flask. Cadmium was then determined electrolytically on 50 cc. portions of the solution.

The results are given in Tables I and II.

TABLE I

Cadmium nitrate ($M/20$) and potassium acid carbonate ($M/20$ to $M/2$)

Conc. of solutions, moles per litre		Molar ratio CO_2/CdO in solutions	Analysis of precipitates, gm.		Molar ratio CdO/CO_2 in precipitates	Average
$Cd(NO_3)_2$	$KHCO_3$		CdO	CO_2		
0.05	0.05	1.0	1.2485	0.4744	1.03	
			1.2685	0.4819	1.03	1.03
0.05	0.25	5.0	1.3115	0.4930	1.037	
			1.2470	0.4806	1.015	1.02
0.05	0.50	10.0	1.2760	0.4888	1.022	
			1.2485	0.4772	1.024	1.02

TABLE II

Cadmium nitrate ($M/20$) and ammonium carbonate ($M/20$ to $M/2$)

Conc. of solutions, moles per litre		Molar ratio CO_2/CdO in solutions	Analysis of precipitates, gm.		Molar ratio CdO/CO_2 in precipitates	Average
$Cd(NO_3)_2$	$(NH_4)_2CO_3$		CdO	CO_2		
0.05	0.05	1.0	1.2100	0.4528	1.046	
			1.2740	0.4684	1.065	
			1.2925	0.4775	1.059	1.06
0.05	0.25	5.0	1.2685	0.4800	1.034	
			1.3300	0.5013	1.036	1.03
0.05	0.50	10.0	1.3070	0.4869	1.050	
			1.3340	0.4960	1.052	1.05

COBALT CARBONATES

Since the normal cobalt carbonate is easily hydrolysed and transformed into basic carbonate, it is difficult to prepare by precipitation even when using potassium acid carbonate. Under the conditions of the present experiments, only one basic carbonate, which has not yet been described, could be obtained.

The solutions used were: cobalt nitrate, $M/20$; potassium acid carbonate $M/10$ to $M/2$. The precipitate obtained with a $M/10$ potassium acid carbonate solution was a basic mixture. More concentrated solutions of the acid carbonate yielded precipitates having the composition $5CoCO_3.Co(OH)_2$.

TABLE III

COBALT NITRATE ($M/20$) AND POTASSIUM ACID CARBONATE ($M/10$ TO $M/2$)

| Conc. of solutions, moles per litre		Molar ratio CO_2/CoO in solutions	Analysis of precipitates, gm.		Molar ratio CoO/CO_2 in precipitates	Average
$Co(NO_3)_2$	$KHCO_3$		CoO	CO_2		
0.05	0.10	2.0	1.6880	0.9935	1.268	1.27
0.05	0.30	6.0	1.4440	0.8862	1.213	
			1.0480	0.6414	1.220	1.22
0.05	0.50	10.0	0.9660	0.6024	1.197	
			0.9545	0.5909	1.206	1.20

TABLE IV

COBALT NITRATE ($M/20$) AND AMMONIUM CARBONATE ($M/40$ TO $M/2$)

Conc. of solutions, moles per litre		Molar ratio CO_2/CoO in solutions	Analysis of precipitates, gm.		Molar ratio CoO/CO_2 in precipitates	Average	Days between precipitation and analysis
$Co(NO_3)_2$	$(NH_4)_2CO_3$		CoO	CO_2			
0.05	0.025	0.5	0.7640	0.2740	2.082	2.10	2
			0.7390	0.2589	2.131		
0.05	0.05	1.0	0.5850	0.1965	2.222		
			0.6810	0.2271	2.239	2.23	5
0.05 (Second precipitation)	0.05	1.0	1.3050	0.4998	1.949		
			1.1765	0.4483	1.959	1.95	1
0.05	0.10	2.0	1.5020	0.6727	1.667		
			1.4135	0.6234	1.693	1.68	1
0.05	0.15	3.0	0.9815	0.4016	1.824		
			0.9910	0.4074	1.816	1.82	1
(Second analysis of same precipitate)			1.2570	0.4094	2.292		
			1.3610	0.4434	2.291	2.29	15
0.05	0.25	5.0	1.3740	0.4933	2.079		
			1.2800	0.4621	2.069	2.07	2
0.05	0.375	7.5	1.4480	0.6158	1.755		
			1.5420	0.6596	1.745	1.75	1
(Second analysis of same precipitate)			1.3035	0.4328	2.248		
			1.4310	0.4728	2.259	2.25	10
0.05	0.50	10.0	1.5355	0.5308	2.159		
			2.1560	0.7616	2.113		
			2.1740	0.7616	2.131	2.13	3

The precipitates obtained with solutions of cobalt nitrate, $M/20$, and of ammonium carbonate, $M/40$ to $M/2$, decomposed rapidly. The curve (Fig. 3) prepared by plotting the time elapsed between filtration and analysis against the value of the CoO/CO_2 molar ratio of each precipitate shows a rapid loss of carbon dioxide during the first five days, and indicates that at equilibrium the value of the molar ratio CoO/CO_2 is more than 2.3.

Other investigators (3) carried out a series of precipitations with solutions of cobalt nitrate, $M/20$, and of normal potassium carbonate, $M/40$ to $M/2$. They obtained indefinite basic carbonates in which the values of the CoO/CO_2 molar ratio were always more than 2. Hence, it can be concluded that the
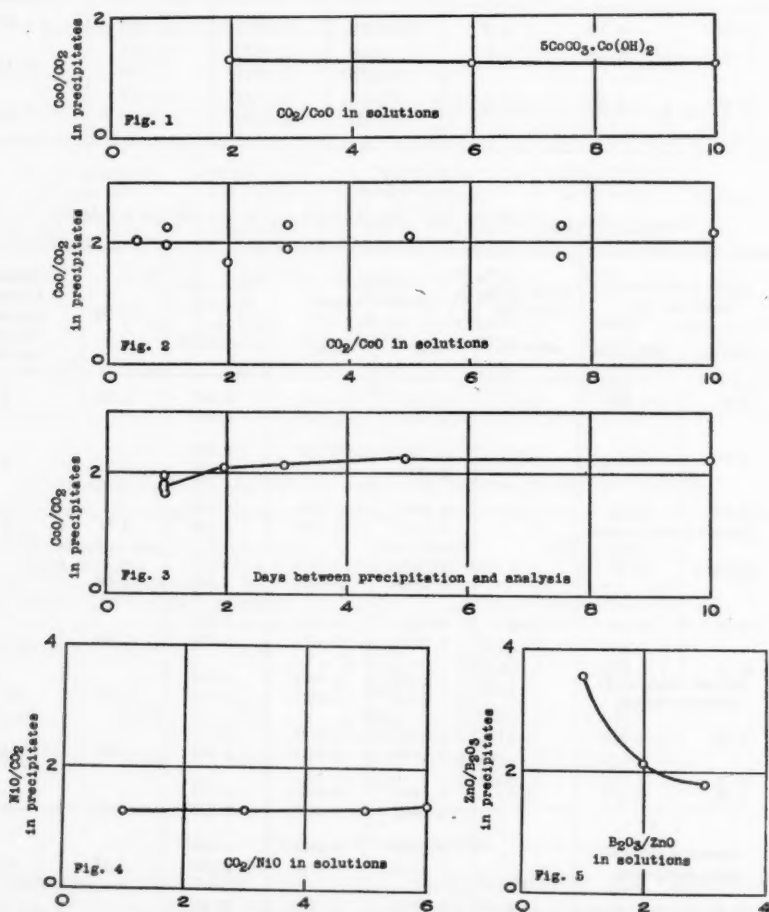
FIGS. 1 - 5. FIG. 1. *Cobalt nitrate and potassium acid carbonate.* FIG. 2. *Cobalt nitrate and ammonium carbonate.* FIG. 3. *Cobalt nitrate and ammonium carbonate.* FIG. 4. *Nickel nitrate and ammonium carbonate.* FIG. 5. *Zinc nitrate and borax.*

composition of the cobalt carbonates, like that of the cadmium carbonates, is greatly influenced by the hydrogen ion concentration.

After filtration, the precipitates were washed thoroughly with cold distilled water and allowed to dry in the air at room temperature. Tests for the presence of potassium or ammonium were negative. The carbon dioxide and the metal were determined on the same portion of the sample: carbon dioxide was displaced with hydrochloric acid and absorbed in weighed soda-lime tubes; cobalt was determined electrolytically.

The results are given in Tables III and IV and Figs. 1, 2, and 3.

NICKEL CARBONATES

Attempts were made to obtain nickel carbonates by treating nickel nitrate solutions with potassium acid carbonate solutions, but the amounts of the precipitates were not sufficient for study.

The solutions used were: nickel nitrate, $M/20$; ammonium carbonate, $M/20$ to $M/2$. When the value of the CO_2/NiO molar ratio in the solutions was less than 7, indefinite basic carbonates were obtained and when the value was more than 7, no precipitate was formed. When using nickel nitrate solutions, $M/20$, and solutions of potassium carbonate, $M/20$ to $3/4$ M, other investigators (3) prepared nickel carbonates that were more basic. Hence, the composition of the nickel carbonates, like that of the carbonates of cadmium and cobalt, depends greatly on the hydrogen ion concentration.

The precipitates were treated and analysed as indicated for the carbonates of cobalt. They contained no ammonium. The results are given in Table V and Fig. 4.

TABLE V

NICKEL NITRATE ($M/20$) AND AMMONIUM CARBONATE ($M/20$ TO $3/10$ M)

Conc. of solutions, moles per litre		Molar ratio CO_2/NiO in solutions	Analysis of precipitates, gm.		Molar ratio NiO/CO_2 in precipitates	Average
$Ni(NO_3)_2$	$(NH_4)_2CO_3$		NiO	CO_2		
0.05	0.05	1.0	0.5800	0.3391	1.282	
			0.5670	0.3304	1.287	1.28
0.05	0.15	3.0	0.9230	0.5324	1.300	
			0.9560	0.5500	1.303	1.30
0.05	0.25	5.0	0.8600	0.4839	1.332	
			0.8980	0.5052	1.332	1.33
0.05	0.30	6.0	0.7810	0.4176	1.402	
			0.8070	0.4316	1.402	1.40

EFFECT OF HYDROGEN ION CONCENTRATION ON THE COMPOSITION OF THE
CARBONATES

It has already been mentioned that the hydrogen ion concentration exerts a
strong influence on the composition of the carbonates of cadmium, cobalt,
and nickel obtained by precipitation. The degree of this influence is indicated
qualitatively in Table VI, in which the results obtained by the authors, with
potassium acid carbonate and ammonium carbonate solutions, are compared
with the results that Cloutier, Pelletier, and Gagnon obtained with normal
potassium carbonate solutions (3). The values of the molar ratio of oxides
in the precipitates increased when the pH values of the mother liquors were
increased.

TABLE VI

COMPOSITION OF THE CARBONATES FOR DIFFERENT pH VALUES

Reactant	Values of the molar ratio of oxides in the precipitates		
	CdO/CO_2	CoO/CO_2	NiO/CO_2
Solutions of low pH values $KHCO_3$	1.0	From 1.22 to 1.27	
Solutions of higher pH values $(NH_4)_2CO_3$	1.0	From 1.75 to 2.29	From 1.28 to 1.40
Solutions of still higher pH values K_2CO_3	From 1.1 to 1.2	From 2.15 to 2.58	From 1.45 to 3.53

BERYLLIUM CHROMATE AND CARBONATES

A few unsuccessful attempts to precipitate beryllium chromate and beryllium
carbonate were made.

When a solution of beryllium nitrate, $M/20$, was used with a potassium
chromate solution, $M/20$, no precipitate was formed. With a $M/4$ solution
of potassium chromate, the precipitate obtained was hydrolysed by washing.
To measure the extent of its decomposition, it was boiled four times with
large quantities of water, filtered off, and analysed by the following method.
It was dissolved in hydrochloric acid, and the solution was treated with an
excess of a sodium hydroxide solution, 6 N, until the precipitate formed at
first redissolved. The solution was then diluted to 500 cc. and boiled for 50
min. The beryllium hydroxide precipitated was filtered off on a hot filter,
washed thoroughly with hot water, dried, ignited, and weighed as BeO. The
chromic acid in the filtrate was determined by iodometric titration. The
results found indicate nearly complete hydrolysis: BeO, 0.3482 gm., CrO_3,
0.0077 gm.; molar ratio, BeO/CrO_3, 181.

Beryllium nitrate solutions treated with either potassium acid carbonate or
ammonium carbonate solutions gave unstable compounds; carbon dioxide
was immediately evolved. These results confirm those of Parsons (11).

Zinc Borates

No definite zinc borate could be obtained under the present experimental conditions.

(a). *Zinc Nitrate and Borax*

Solutions of zinc nitrate $M/20$, and of borax, B_2O_3 $M/20$ to $3/20$ M, were used. Indefinite basic borates were obtained. When the concentrations of the solutions of borax were increased, the precipitates became less basic. The pH values of the mother liquors were determined within 0.2. It was thus established that the more basic precipitate of this series was formed in a slightly acid medium, whereas the others were formed in a slightly alkaline medium. This was probably due to the solubility of zinc hydroxide in the sodium hydroxide formed by the hydrolysis of borax.

For analysis, the precipitates were filtered off, washed thoroughly with cold distilled water, and dried at red heat. A weighed portion was fused with a mixture of potassium and sodium carbonates. The melt was digested with distilled water on the water-bath until disintegration was complete. The zinc carbonate was filtered off, washed with 1% solution of sodium carbonate and then with cold distilled water, dried, ignited, and weighed as ZnO. The filtrate was acidified, refluxed to remove all the carbon dioxide, and diluted to 250 cc. with freshly boiled distilled water. A 50 cc. portion was neutralized with a sodium hydroxide solution, $N/10$, using methyl orange as indicator. Another 50 cc. portion of the borate solution was neutralized, without methyl orange, by the addition of the same volume of standard sodium hydroxide solution, $N/10$. The boric acid was titrated by further addition of standard sodium hydroxide solution in the presence of neutral glycerol and phenolphtalein as indicator. Later it was found sufficient to determine ZnO by the pyrophosphate method and B_2O_3 by difference. The precipitates contained no sodium.

The results are given in Table VII and Fig. 5.

TABLE VII

ZINC NITRATE ($M/20$) AND BORAX (B_2O_3 $M/20$ TO $3/20$ M)

Conc. of solutions, moles per litre		Molar ratio B_2O_3/ZnO in solutions	Analysis of precipitates, gm.		Molar ratio ZnO/B_2O_3 in precipitates	Average	pH values of the mother liquors
Zn(NO₃)₂	B₂O₃(borax)		ZnO	B₂O₃			
0.05	0.05	1.0	1.2024	0.2911	3.53	3.53	6.6
0.05	0.10	2.0	0.4005	0.1611*	2.127		
			0.3217	0.1305*	2.110	2.12	7.8
0.05	0.15	3.0	1.2746	0.6100	1.788	1.79	7.8

* *By difference.*

(b). Zinc Nitrate, Borax, and Sodium Hydroxide

The authors used four litres of zinc nitrate solutions, $M/20$, and solutions made up of two litres of borax solutions, B_2O_3 $M/20$, and two litres of sodium hydroxide solutions of different concentrations, Na_2O $M/20$ to $M/5$. Another precipitation was made in which boric acid, $M/10$, was used instead of sodium hydroxide. All the precipitates were basic and the basicity was found to increase very quickly with the alkalinity of the medium. When the value of the molar ratio of oxides, Na_2O/ZnO, in the solutions reached 4.0, the precipitate consisted almost entirely of zinc hydroxide. This can be explained by the law of mass action. The addition of sodium hydroxide prevents the hydrolysis of the borax.

The pH values of the mother liquors were determined within 0.2. The precipitates were treated and analysed as indicated above. They contained no sodium.

The results are given in Table VIII and Fig. 6, together with the results of an experiment with a zinc nitrate solution, $M/20$, and a borax solution, $M20$.

TABLE VIII

ZINC NITRATE ($M/20$), BORAX (B_2O_3 $M/20$), SODIUM HYDROXIDE (Na_2O $M/20$ TO $M/5$), AND BORIC ACID (B_2O_3 $M/10$)

Conc. of solutions, moles per litre			Molar ratio Na_2O/ZnO in solutions	Analysis of precipitates, gm.		Molar ratio ZnO/B_2O_3 in precipitates	Average	pH values of the mother liquors
$Zn(NO_3)_2$ 4 litres	B_2O_3 (borax) 2 litres	Na_2O 2 litres		ZnO	B_2O_3			
0.05	0.05	0.05	0.5	1.6176	0.2598*	5.328	5.33	6.6
0.05	0.05	0.10	1.0	1.5272	0.0522	25.03	25.0	9.2
0.05	0.05	0.20	2.0	1.4086	0.0045	269.06	269	9.6
		B_2O_3 (boric ac.) 2 litres	Molar ratio B_2O_3(bor. ac.) ZnO in solutions					
0.05	0.05	0.10	1.0	0.3986 0.3572	0.1278* 0.1148	2.669 2.663	2.67	6.8
0.05	0.05	—	0.0	1.2024	0.2911	3.53	3.53	6.6

* By difference.

COPPER SILICATES

(a). Copper Sulphate and Sodium Metasilicate

Solutions of copper sulphate, $M/20$, and of sodium metasilicate, Na_2SiO_3, $M/40$ to $M/2$, were used. Indefinite basic and acid copper silicates were obtained.

The precipitates formed were filtered off immediately. They were gelatinous and could not be filtered rapidly. They were washed with distilled water until the filtrate gave no brown precipitate or colour with silver nitrate solution. All were pale blue but some darkened and became greenish during washing and drying. After drying at 80°, they were powdered and analysed.
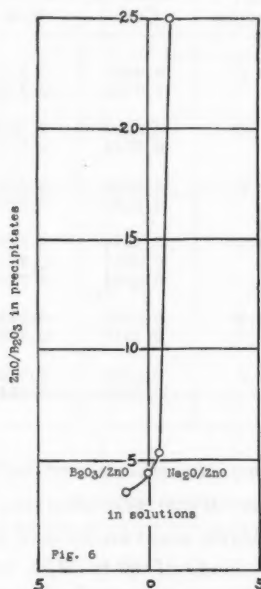
FIG. 6. *Zinc nitrate, borax, sodium hydroxide and boric acid.*

The material (1.5 gm.) was weighed into a small porcelain dish and covered with water. Concentrated hydrochloric acid (5 cc.) was added and the solution evaporated to dryness on the water-bath. The addition of concentrated hydrochloric acid and evaporation to dryness were repeated twice. The mass was then moistened with concentrated hydrochloric acid and allowed to stand for 15 min. After addition of hot water, the silica was filtered off and washed with hot water until free from hydrochloric acid. The filtrate was evaporated to dryness and the residue treated as the original material. The two filter papers were dried and ignited together in a weighed platinum crucible in the electric furnace at red heat. The silica was then weighed. It was almost pure silica, leaving virtually no residue when treated with hydrofluoric acid.

The filtrate containing the copper was treated with concentrated sulphuric acid (3 cc.), evaporated on the water-bath, and diluted to exactly 100 cc. Copper was then determined by electrolysis on an aliquot portion. The precipitates contained no sodium.

The results are given in Table IX and Fig. 7.

TABLE IX

COPPER SULPHATE ($M/20$) AND SODIUM METASILICATE ($M/40$ TO $M/2$)

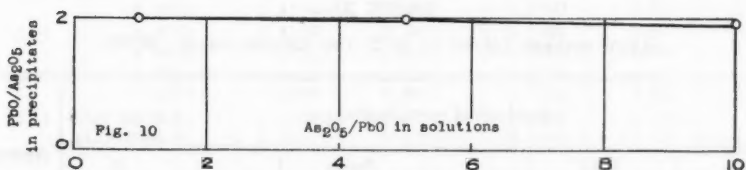| Conc. of solutions, moles per litre		Molar ratio SiO_2/CuO in solutions	Analysis of precipitates, gm.		Molar ratio CuO/SiO_2 in precipitates	Average
$CuSO_4$	Na_2SiO_3		CuO	SiO_2		
0.05	0.025	0.5	0.9423	0.2216	3.210	
			0.9788	0.2322	3.182	3.20
0.05	0.05	1.0	0.8004	0.5076	1.187	
			0.9132	0.5812	1.186	1.19
0.05	0.10	2.0	0.8206	0.5726	1.082	
			0.8151	0.5706	1.078	1.08
0.05	0.15	3.0	0.6424	0.5294	0.916	
			0.6053	0.4926	0.928	
			0.6654	0.5554	0.904	0.92
0.05	0.25	5.0	0.7350	0.5854	0.948	
			0.7515	0.5982	0.948	0.95
0.05	0.50	10.0	0.6294	0.6256	0.759	
			0.6349	0.6442	0.744	0.75

(b) *Copper Sulphate, Sodium Metasilicate, and Sodium Hydroxide*

Copper sulphate solution, $M/20$, and solutions made up of two litres of sodium silicate solutions, $M/20$, and two litres of sodium hydroxide solutions of different concentrations, Na_2O $M/40$ to $M/4$, were used. Indefinite basic silicates were obtained. The precipitates had apparently the same physical properties as those of the preceding series, and were treated and analysed in the same way. They contained no sodium. The results are given in Table X.

TABLE X

COPPER SULPHATE ($M/20$), SODIUM METASILICATE ($M/20$), AND SODIUM HYDROXIDE (Na_2O $M/40$ TO $M/4$)

Conc. of solutions, moles per litre			Molar ratio Na_2O/CuO in solutions	Analysis of precipitates, gm.		Molar ratio CuO/SiO_2 in precipitates	Average
$CuSO_4$ 4 litres	Na_2SiO_3 2 litres	Na_2O 2 litres		CuO	SiO_2		
0.05	0.05	0.025	0.25	1.0249	0.2478	3.122	
				0.9708	0.2368	3.095	3.11
0.05	0.05	0.125	1.25	1.1015	0.2332	3.565	
				1.0990	0.2320	3.575	3.57
0.05	0.05	0.25	2.5	1.1175	0.1992	4.235	
				1.1290	0.2010	4.240	4.24

Fig. 7 SiO_2/CuO in solutions   (y-axis: CuO/SiO_2 in precipitates)

Fig. 8 As_2O_5/PbO in solutions   (y-axis: PbO/As_2O_5 in precipitates)

Fig. 9 As_2O_5/PbO in solutions   (y-axis: PbO/As_2O_5 in precipitates)

Fig. 10 As_2O_5/PbO in solutions   (y-axis: PbO/As_2O_5 in precipitates)
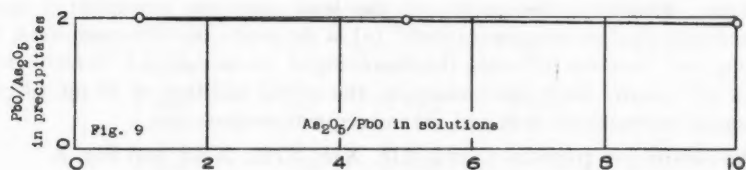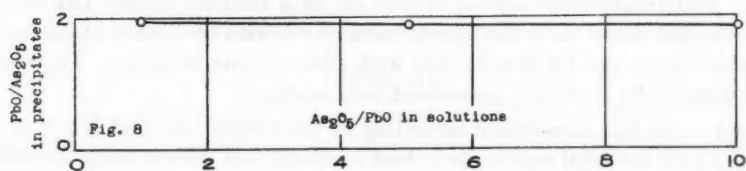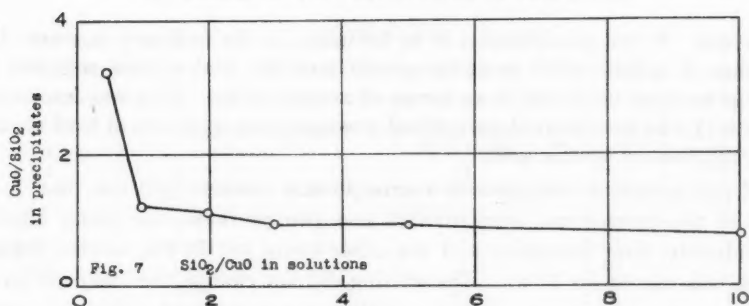
FIGS. 7 - 10. FIG. 7. *Copper sulphate and sodium metasilicate.* FIG. 8. *Lead nitrate and arsenic oxide.* FIG. 9. *Lead nitrate and monopotassium arsenate.* FIG. 10. *Lead acetate and arsenic oxide.*

LEAD ARSENATES

(a) *Lead Nitrate and Arsenic Acid*

Solutions of arsenic oxide, $M/20$, and of lead nitrate, $M/10$ to $M/2$, were used. Pure dilead arsenate was always obtained.

With solutions of lead nitrate, $M/20$, and of arsenic oxide, $M/20$ to $M/2$, precipitates that were more acidic were formed. They probably consisted of dilead arsenate, $PbHAsO_4$, with adsorbed arsenate ions, since the acidity of the precipitates increased with the excess of arsenic oxide used.

These results show clearly that if pure dilead arsentate is to be precipitated from solutions of lead nitrate and arsenic oxide, the arsenic oxide must not be

in excess. If the precipitation is to be made in the ordinary manner, the solution of arsenic oxide must be poured into the lead nitrate solution, so that at no time there can be an excess of arsenic oxide. This was known by Rose (17) who precipitated pure dilead arsenate from solutions of lead nitrate with solutions of arsenic acid.

All precipitations took place in a strongly acid medium (pH less than 1.7). Two of the precipitates were divided into two portions, one being filtered immediately after formation and the other being left in the mother liquor, which was stirred for 24 hr. The stirring did not change the composition of the arsenates; this indicated that equilibrium was attained quickly in every case. Precipitates were always filtered off on a Büchner funnel and washed with distilled water until the filtrate gave no reaction for lead with hydrogen sulphide water, nor for arsenic acid with silver nitrate solution. They were then dried at 80 to 90° C., pulverized, and analysed.

Lead oxide was determined according to the Official Method No. 1 of the A.O.A.C. (1) for total lead oxide in lead arsenate, and arsenic oxide according to the Tentative Method of the A.O.A.C. (1) for total arsenic oxide in lead arsenate. However, the purity of the lead arsenates precipitated made unnecessary the following operations: (a) in the lead oxide determination, the heating and filtration following the dissolving of the sample in 1 : 4 nitric acid; (b) in the arsenic oxide determination, the initial addition of 25 ml. of concentrated hydrochloric acid and the subsequent evaporation.

The results are given in Tables XIa, XIb, XIIa, XIIb, and Fig. 8.

TABLE XIa

LEAD NITRATE ($M/10$ TO $M/2$) AND ARSENIC OXIDE ($M/20$)

Precipitate No.	Analysis of precipitates, gm.				Molar ratio PbO/As_2O_5 in precipitates	Average
	PbO determination samples	PbO	As_2O_5 determination samples	As_2O_5		
55-1	0.5020	0.3226	0.5012	0.1656	2.00	
	0.5049	0.3242	0.5024	0.1660	2.00	2.00
56-1	0.5004	0.3220	0.5082	0.1657	2.03	
	0.5035	0.3236	0.5056	0.1643	2.03	2.03
56-11	0.5249	0.3360	0.5253	0.1729	2.00	
	0.5499	0.3529	0.5253	0.1735	2.00	2.00
57-1	0.5131	0.3294	0.4913	0.1615	2.01	
	0.4897	0.3131	0.5108	0.1681	2.00	2.01
57-11	0.4938	0.3160	0.5062	0.1664	2.00	
	0.5558	0.3539	0.4982	0.1640	1.99	2.00

TABLE XI*b*

LEAD NITRATE ($M/10$ TO $M/2$) AND ARSENIC OXIDE ($M/20$)

Precipitate No.	Conc. of solutions, moles per litre		Molar ratio PbO/As_2O_5 in solutions	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors
	$Pb(NO_3)_2$	As_2O_5			
55-1	0.10	0.05	2.0	2.00	1.2
56-1	0.25	0.05	5.0	2.03	1.1
56-11	0.25	0.05	5.0	2.00	
57-1	0.50	0.05	10.0	2.01	1.0
57-11	0.50	0.05	10.0	2.00	

1 : *filtered immediately after precipitation.*
11 : *filtered after stirring 24 hr. in the mother liquor.*

TABLE XII*a*

LEAD NITRATE ($M/20$) AND ARSENIC OXIDE ($M/20$ TO $M/2$)

Precipitate No.	Analysis of precipitates, gm.				Molar ratio PbO/As_2O_5 in precipitates	Average
	PbO determination samples	PbO	As_2O_5 determination samples	As_2O_5		
51-1	0.5004	0.3161	0.5002	0.1673	1.94	
	0.5006	0.3176	0.5006	0.1679	1.95	1.95
51-11	0.5004	0.3194	0.5020	0.1671	1.97	
	0.5000	0.3188	0.5028	0.1676	1.97	1.97
52-1	0.5000	0.3122	0.5016	0.1703	1.89	
	0.5002	0.3104	0.5000	0.1700	1.88	1.89
52-11	0.5007	0.3102	0.5015	0.1709	1.87	
	0.5002	0.3111	0.5001	0.1702	1.88	1.88
53-1	0.5007	0.3040	0.5015	0.1724	1.82	
	0.5008	0.3049	0.5011	0.1721	1.82	1.82
53-11	0.5024	0.3083	0.4054	0.1398	1.83	
	0.5011	0.3067	0.4002	0.1378	1.83	1.83

TABLE XII*b*

LEAD NITRATE ($M/20$) AND ARSENIC OXIDE ($M/20$ TO $M/2$)

Precipitate No.	Conc. of solutions, moles per litre		Molar ratio As_2O_5/PbO in solutions	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors
	$Pb(NO_3)_2$	As_2O_5			
51-1	0.05	0.05	1.0	1.95	1.7
51-11	0.05	0.05	1.0	1.97	
52-1	0.05	0.25	5.0	1.89	1.7
52-11	0.05	0.25	5.0	1.88	
53-1	0.05	0.50	10.0	1.82	1.2
53-11	0.05	0.50	10.0	1.83	

1 : *filtered immediately after precipitation.*
11 : *filtered after stirring 24 hr. in the mother liquor.*

(b) Lead Nitrate and Monopotassium arsenate

Solutions of lead nitrate, $M/20$, and of monopotassium arsenate, KH_2AsO_4, $M/10$ to M, were used. The monopotassium arsenate solution was prepared by mixing solutions of arsenic acid and of potassium hydroxide in equivalent quantities.

The first precipitation with monopotassium arsenate, $M/10$, gave pure dilead arsenate. The other two experiments, in which greater excesses of monopotassium arsenate were used, yielded precipitates that are more acidic and that are believed to consist of dilead arsenate with adsorbed arsenate ions. A slight excess of monopotassium arsenate may be used to prepare pure dilead arsenate from lead nitrate solutions whereas, as indicated above, if a slight excess of arsenic acid is present, the precipitate is not pure. In any case, it is safer to have an excess of lead nitrate present. McDonnell and Smith precipitated pure dilead arsenate from solutions of lead nitrate and solutions of monopotassium arsenate (13).

The precipitates were filtered off immediately after formation. They were treated and analysed as described before. None contained potassium. The mother liquors were all strongly acid (pH less than 3.2). The results are given in Tables XIIIa and XIIIb and in Fig. 9.

TABLE XIIIa

LEAD NITRATE ($M/20$) AND MONOPOTASSIUM ARSENATE ($M/10$ TO M)

Precipitate No.	Analysis of precipitates, gm.				Molar ratio PbO/As_2O_5 in precipitates	Average
	PbO determination samples	PbO	As_2O_5 determination samples	As_2O_5		
84	0.5194	0.3358	0.4957	0.1642	2.01	
	0.5351	0.3459	0.5618	0.1851	2.02	2.01
85	0.5093	0.3242	0.5133	0.1730	1.94	
	0.4954	0.3160	0.5230	0.1761	1.95	1.95
86	0.5012	0.3166	0.4874	0.1655	1.91	
	0.4798	0.3028	0.4869	0.1653	1.91	1.91

TABLE XIIIb

LEAD NITRATE ($M/20$) AND MONOPOTASSIUM ARSENATE ($M/10$ TO M)

Precipitate No.	Conc. of solutions, moles per litre			Molar ratio As_2O_5/PbO in solutions	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors
	$Pb(NO_3)_2$ 4 litres	As_2O_5 2 litres	K_2O 2 litres			
84	0.05	0.10	0.10	1.0	2.01	2.0
	0.05	0.50	0.50	5.0	1.95	2.8
86	0.05	1.00	1.00	10.0	1.91	3.2

(c) *Lead Acetate and Arsenic Acid*

The solutions used were: lead acetate, $M/20$; arsenic oxide, $M/20$ to $M/2$. With the $M/20$ solution of arsenic oxide pure dilead arsenate was obtained. With the others, the precipitates were more acid and consisted probably of dilead arsenate with adsorbed arsenate ions. Arsenic oxide when not in greater excess than twice the equivalent quantity will precipitate pure dilead arsenate from lead acetate solutions, whereas with lead nitrate solutions such an excess yielded an impure product.

All precipitates were formed in a strongly acid medium (pH under 2.1). They were filtered off immediately, treated, and analysed as mentioned before.

The results are given in Tables XIV*a* and XIV*b* and Fig. 10.

TABLE XIV*a*

LEAD ACETATE ($M/20$) AND ARSENIC OXIDE ($M/20$ TO $M/2$)

Precipitate No.	Analysis of precipitates, gm.				Molar ratio PbO/As_2O_5 in precipitates	Average
	PbO determination samples	PbO	As_2O_5 determination samples	As_2O_5		
66	0.5386	0.3479	0.5167	0.1720	1.99	
	0.5106	0.3298	0.5169	0.1722	1.99	1.99
67	0.4776	0.3046	0.4789	0.1607	1.96	
	0.4894	0.3135	0.4965	0.1666	1.97	1.96
68	0.5198	0.3320	0.5013	0.1697	1.94	
	0.4981	0.3177	0.5325	0.1801	1.94	1.94

TABLE XIV*b*

LEAD ACETATE ($M/20$) AND ARSENIC OXIDE ($M/20$ TO $M/2$)

Precipitate No.	Conc. of solutions, moles per litre		Molar ratio As_2O_5/PbO in solutions	Molar ratio PbO/As_2O_5 in precipitates	pH value of mother liquors
	$Pb(C_2H_3O_2)_2$	As_2O_5			
66	0.05	0.05	1	1.99	2.1
67	0.05	0.25	5	1.96	1.5
68	0.05	0.50	10	1.94	1.5

(d) *Lead Chloride and Arsenic Acid*

Solutions of lead chloride, $M/30$, and of arsenic oxide, $M/30$ to $M/2$, were used. Indefinite lead chloroarsenates were formed. McDonnell and Smith (15) prepared a lead chloroarsenate having nearly the same composition as mimetite, $Pb_4(PbCl)(AsO_4)_3$, the only difference being in its chlorine content,

which was slightly higher than in mimetite. The first precipitation of this series with arsenic oxide, $M/30$, gave also a chloroarsenate with a composition close to that of mimetite, although the chlorine content is still higher than that of the chloroarsenate prepared by McDonnell and Smith. Gmelin (5, p. 173) states that dilead arsenate is the product of the reaction of lead chloride and arsenic acid or a soluble arsenate. McDonnell and Smith (13) say that a chloroarsenate is usually formed but that dilead arsenate can also be formed. No definite lead chloroarsenate nor dilead arsenate were obtained in the present experiments. All the mother liquors were strongly acid (pH less than 1.6).

As soon as formed, the precipitates were filtered off, thoroughly washed, and dried at 80° C. Arsenic oxide and lead oxide were determined by the methods already mentioned, and chlorine, by means of silver nitrate, on 0.5 gm. of precipitate dissolved in dilute nitric acid.

The results are given in Table XV and Fig. 11.

TABLE XV

LEAD CHLORIDE ($M/30$) AND ARSENIC OXIDE ($M/30$ TO $M/3$)

Conc. of solutions, moles per litre		Molar ratio As_2O_5/PbO in solutions	Analysis of precipitates, %				Total
$PbCl_2$	As_2O_5		PbO	As_2O_5	Cl	Minus oxygen equiv. to Cl	
0.033	0.033	1.0	74.65	22.86	2.91	0.66	99.76
			74.66	22.84	2.92	0.66	99.76
0.033	0.166	5.0	72.72	24.40	2.70	0.61	99.21
			72.55	24.38	2.70	0.61	99.02
0.033	0.333	10.0	69.75	27.60	1.82	0.41	98.76
			69.84	27.59	1.82	0.41	98.84
Composition of mimetite $Pb_4(PbCl)(AsO_4)_3$:			74.99	23.17	2.38	0.54	100.00
Composition of McDonnell and Smith's lead chloroarsenate:			74.64	22.81	2.72	0.61	99.56

(e) Lead Nitrate and Dipotassium Arsenate

Solutions of lead nitrate, $M/20$, and of dipotassium arsenate, K_2HAsO_4, $M/20$ to M, were used. The dipotassium arsenate solutions were prepared by mixing solutions of arsenic acid with those of potassium hydroxide in equivalent quantities. The precipitation with the $M/20$ dipotassium arsenate took place in a strongly acid medium and yielded dilead arsenate. With more concentrated solutions of dipotassium arsenate, the pH values were higher and the precipitates became more basic. Trilead arsenate, $Pb_3(AsO_4)_2$, was obtained when the values of the molar ratio As_2O_5/PbO in the solutions were between 2.5 and 4.0 at a pH of 7.45–7.6.
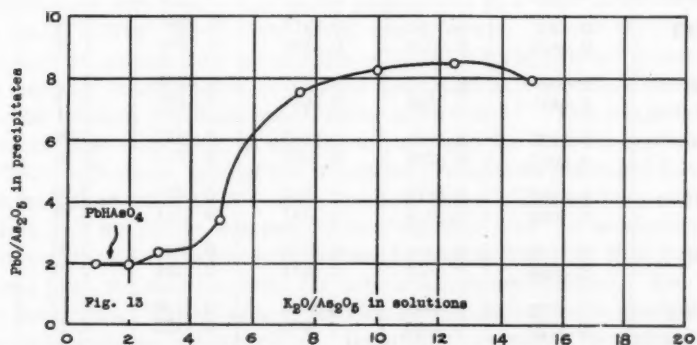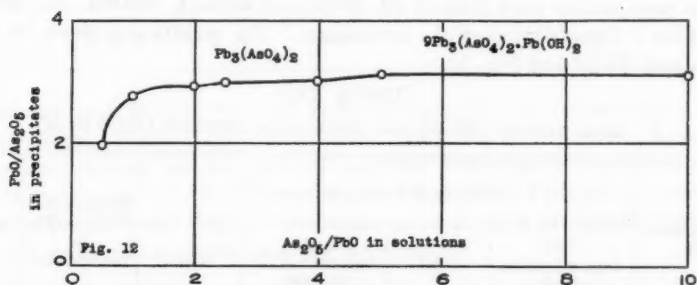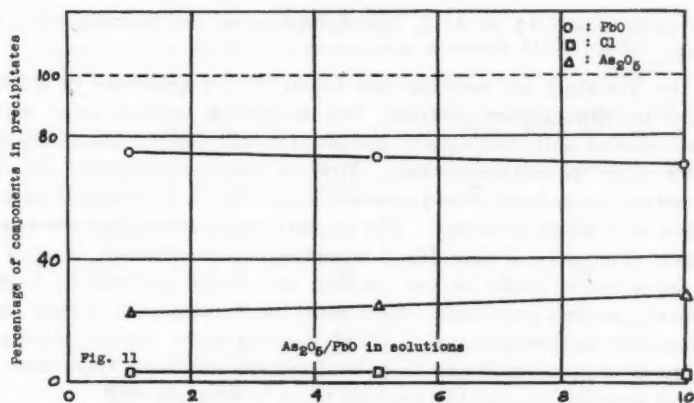
FIGS. 11 - 13.   FIG. 11. *Lead chloride and arsenic oxide.*   FIG. 12. *Lead nitrate and dipotassium arsenate.*   FIG. 13. *Lead nitrate, arsenic oxide, and potassium hydroxide.*

These results confirm those of McDonnell and Smith (14) who found that trilead arsenate exists in solution only under specific conditions as an intermediate product between dilead arsenate and a basic arsenate.

The experiments made with great excess of arsenate yielded a definite compound, which has not yet been described.   The value of its PbO/As_2O_5

molar ratio was 3.11 to 3.12, corresponding to the formula $9Pb_3(AsO_4)_2 \cdot Pb(OH)_2$.

In the literature no mention was found of precipitations of a lead salt solution by dipotassium arsenate, but numerous authors have used lead nitrate solution with solutions of the sodium salt, Na_2HAsO_4, which is more common than the potassium salt. Most of these investigators (13, 22, 19) obtained a slightly basic dilead arsenate but a few (4, 6) prepared pure dilead arsenate with dilute solutions. The present results show that there must be no excess of arsenate if pure dilead arsenate is to be obtained, because otherwise the solution would be too alkaline and would prevent its formation. Moreover, as seen previously, there must be no excess of arsenic oxide in solution since the precipitate will adsorb arsenate ions. Briefly, if pure dilead arsenate is to be precipitated from lead nitrate solutions, there must be no excess of arsenate ion and the medium must be strongly acid.

The precipitates were filtered off as soon as formed, treated, and analysed as before. They contained no potassium. The results are given in Tables XVIa and XVIb and Fig. 12.

TABLE XVIa

LEAD NITRATE ($M/20$) AND DIPOTASSIUM ARSENATE ($M/20$ TO M)

Precipitate No.	Analysis of precipitates, gm.				Molar ratio PbO/As_2O_5 in precipitates	Average
	PbO determination samples	PbO	As_2O_5 determination samples	As_2O_5		
63-1	0.4837	0.3084	0.4812	0.1597	1.98	
	0.4820	0.3079	0.4798	0.1596	1.98	1.98
88	0.4891	0.3531	0.4811	0.1294	2.76	
	0.4851	0.3503	0.5019	0.1355	2.75	2.76
90	0.5139	0.3762	0.5133	0.1332	2.90	
	0.5061	0.3704	0.5307	0.1373	2.91	2.91
77	0.5618	0.4118	0.5057	0.1278	2.98	
	0.5066	0.3713	0.5187	0.1313	2.98	2.98
91	0.5102	0.3761	0.4976	0.1252	3.02	
	0.4884	0.3601	0.5016	0.1264	3.01	3.02
78	0.5322	0.3955	0.5014	0.1230	3.12	
	0.5120	0.3802	0.5092	0.1253	3.11	3.11
87	0.5361	0.3965	0.5003	0.1223	3.11	
	0.5206	0.3853	0.5111	0.1250	3.12	3.12

(*f*) *Lead Nitrate, Arsenic Acid and Potassium Hydroxide*

Solutions of lead nitrate, $M/20$, and solutions made up of two litres of arsenic oxide solutions, $M/20$, and two litres of potassium hydroxide solutions of different concentrations, K_2O $M/20$ to $3/4 M$, were used. The first

TABLE XVI*b*

LEAD NITRATE ($M/20$) AND DIPOTASSIUM ARSENATE ($M/20$ TO M)

Precipitate No.	Conc. of solutions, moles per litre			Molar ratio As_2O_5/PbO in solutions	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors
	$Pb(NO_3)_2$ 4 litres	As_2O_5 2 litres	K_2O 2 litres			
63-1	0.05	0.05	0.10	0.5	1.98	2.0
88	0.05	0.10	0.20	1.0	2.76	6.8
90	0.05	0.20	0.40	2.0	2.91	7.4
77	0.05	0.25	0.50	2.5	2.98	7.45
91	0.05	0.40	0.80	4.0	3.02	7.6
78	0.05	0.50	1.00	5.0	3.11	7.8
87	0.05	1.00	2.00	10.0	3.12	9.0

experiments with dilute potassium hydroxide gave dilead arsenate in a strongly acid medium. With more concentrated solutions of potassium hydroxide, the mother liquors became alkaline and the precipitates more basic. The definite compound, $Pb_5(PbOH)_2(AsO_4)_4$ or $2Pb_3(AsO_4)_2.Pb(OH)_2$, prepared by McDonnell and Smith (16) by the action of sodium or potassium hydroxide solutions on dilead arsenate, was not precipitated.

Moreover, investigations suggested by results obtained by Strömholm (21) led McDonnell and Smith (16) to the preparation of a basic arsenate of lead $8PbO.As_2O_5.1/2H_2O$, which they called octo-arsenate. One of their methods of preparation consisted in the addition of a lead nitrate solution in successive equal portions to a solution of sodium hydroxide and trisodium arsenate in which the value of the Na_2O/As_2O_5 molar ratio was 15. The precipitate was filtered off after each addition and the filtrate used for the next precipitation. The PbO/As_2O_5 molar ratio of the successive precipitates decreased from high values to values close to 8.4 and remained there. The authors concluded that free lead hydroxide was precipitated together with the octo-arsenate at first, and then, when the excess of sodium hydroxide had been thus somewhat removed from the solution, only the octo-arsenate precipitated. The values of the molar ratio, Na_2O/As_2O_5, in solution corresponding to the precipitations of the octo-arsenate are not given. In other experiments the values of the PbO/As_2O_5 molar ratio in the octo-arsenate ranged from 7.94 to 8.20, the average being 8.07. It is evident that the octo-arsenate is not a very well defined compound.

For three precipitations in the present experiments, the values of the PbO/As_2O_5 molar ratio in the precipitates lie between 7.95 and 8.44, which corresponds with the values found by McDonnell and Smith for their octo-arsenate, but it cannot be said whether a definite compound was formed.

Before analysis, each precipitate was divided into two portions, one was dried immediately at 80° C., the other, after having been left in the mother liquor, which was stirred for 24 hr. No great difference in composition was noted between the two portions.

TABLE XVII*a*

LEAD NITRATE ($M/20$), ARSENIC OXIDE ($M/20$), AND POTASSIUM HYDROXIDE
(K_2O $M/20$ TO $3/4$ M)

Precipitate No.	Analysis of precipitates, gm.				Molar ratio PbO/As_2O_5 in precipitates	Average
	PbO determination samples	PbO	As_2O_5 determination samples	As_2O_5		
58-1	0.5041	0.3220	0.4884	0.1610	1.99	
	0.5053	0.3210	0.5025	0.1657	1.98	1.99
58-11	0.5047	0.3219	0.5225	0.1721	1.99	
	0.4965	0.3167	0.4884	0.1613	1.99	1.99
63-1	0.4837	0.3084	0.4812	0.1597	1.98	
	0.4820	0.3079	0.4798	0.1596	1.98	1.98
63-11	0.5030	0.3222	0.5350	0.1767	2.00	
	0.4848	0.3078	0.5276	0.1744	1.98	1.99
61-1	0.4956	0.3366	0.4985	0.1487	2.34	
	0.4953	0.3362	0.4915	0.1466	2.34	2.34
61-11	0.4936	0.3260	0.5002	0.1553	2.19	
	0.4969	0.3276	0.5095	0.1585	2.18	2.19
59-1	0.4896	0.3671	0.4823	0.1099	3.39	
	0.4940	0.3694	0.4956	0.1130	3.38	3.38
59-11	0.5671	0.4226	0.5148	0.1177	3.36	
	0.5229	0.3925	0.5378	0.1233	3.37	3.36
62-1	0.4829	0.4187	0.5557	0.0660	7.52	
	0.4831	0.4186	0.4787	0.0570	7.49	7.51
62-11	0.5043	0.4270	0.4897	0.0601	7.11	
	0.4855	0.4154	0.4825	0.0593	7.17	7.14
60-1	0.5243	0.4525	0.4861	0.0533	8.24	
	0.4816	0.4217	0.5495	0.0597	8.30	8.27
60-11	0.4979	0.4402	0.5198	0.0595	8.31	
	0.5057	0.4471	0.4814	0.0529	8.29	8.30
65-1	0.4840	0.4280	0.4784	0.0518	8.41	
	0.4823	0.4303	0.4814	0.0522	8.47	8.44
65-11	0.4884	0.4357	0.4969	0.0546	8.37	
	0.5004	0.4469	0.5220	0.0573	8.38	8.37
64-1	0.4970	0.4072	0.5028	0.0534	7.95	
	0.4778	0.3916	0.5126	0.0544	7.96	7.95
64-11	0.4843	0.4179	0.4936	0.0536	8.19	
	0.4825	0.4168	0.5172	0.0563	8.17	8.18

Each portion was washed and analysed as already described. All the arsenates were free from potassium.

The results are given in Tables XVII*a* and XVII*b* and Fig. 13.

TABLE XVII*b*

LEAD NITRATE ($M/20$), ARSENIC OXIDE ($M/20$) AND POTASSIUM HYDROXIDE
(K_2O $M/20$ TO $3/4$ M)

Precipitate No.	Conc. of solutions, moles per litre			Molar ratio K_2O/As_2O_5 in solutions	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors
	$Pb(NO_3)_2$ 4 litres	As_2O_5 2 litres	K_2O 2 litres			
58-1	0.05	0.05	0.05	1.0	1.99	1.7
58-11	0.05	0.05	0.05	1.0	1.99	1.65
63-1	0.05	0.05	0.10	2.0	1.98	2.0
63-11	0.05	0.05	0.10	2.0	1.99	
61-1	0.05	0.05	0.15	3.0	2.34	7.35
61-11	0.05	0.05	0.15	3.0	2.19	7.25
59-1	0.05	0.05	0.25	5.0	3.38	
59-11	0.05	0.05	0.25	5.0	3.36	10.2
62-1	0.05	0.05	0.375	7.5	7.51	
62-11	0.05	0.05	0.375	7.5	7.14	12.0
60-1	0.05	0.05	0.50	10.0	8.27	12.55
60-11	0.05	0.05	0.50	10.0	8.30	12.45
65-1	0.05	0.05	0.625	12.5	8.44	12.8
65-11	0.05	0.05	0.625	12.5	8.37	
64-1	0.05	0.05	0.75	15.0	7.95	12.8
64-11	0.05	0.05	0.75	15.0	8.18	12.75

1 : *filtered immediately after precipitation.*
11 : *filtered after stirring 24 hr. in the mother liquor.*

(g) *Lead Nitrate, Arsenic Acid, and Ammonium Hydroxide*

Solutions of lead nitrate, $M/20$, and solutions made up of two litres of arsenic oxide solutions, $M/20$, and two litres of ammonium hydroxide solutions of different concentrations, $M/20$ to M, were used.

With the two most dilute solutions of ammonium hydroxide, dilead arsenate was precipitated in strongly acid liquors. Then, as the alkalinity increased, the molar ratio, PbO/As_2O_5, in the precipitates rose to 3.25 and remained there, indicating the formation of a definite compound: $4Pb_3(AsO_4)_2.Pb(OH)_2$.

The definite compound, $Pb_4(PbOH)(AsO_4)_3$ or $3Pb_3(AsO_4)_2 Pb(OH)_2$, prepared by different authors by the action of ammonium hydroxide on dilead arsenate (13, 16, 19) was not formed, even when the mother liquors were stirred for 24 hr. before filtration. Streeter and Thatcher (20) could not prepare this compound when they repeated all the experiments given in the literature.

The precipitates were washed thoroughly, dried, and analysed as described before.   They contained no ammonium.

The results are given in Tables XVIII*a* and XVIII*b* and Fig. 14.

TABLE XVIII*a*

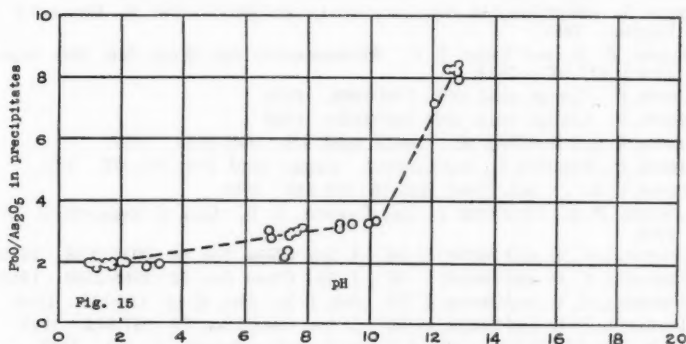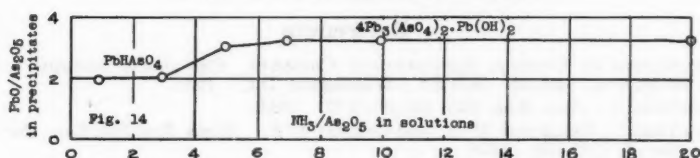Lead nitrate ($M/20$), arsenic oxide ($M/20$), and ammonium hydroxide ($M/20$ to M)

Precipitate No.	Analysis of precipitates				Molar ratio PbO/As_2O_5 in precipitates	Average
	PbO determination samples	PbO	As_2O_5 determination samples	As_2O_5		
74[1]		% 64.71 64.75 64.73		% 33.51 33.45 33.48		1.98
70	gm. 0.4961 0.5290	gm. 0.3221 0.3432	gm. 0.4795 0.5166	gm. 0.1588 0.1771	2.02 2.02	2.02
69	0.5626 0.5201	0.4193 0.3881	0.4807 0.5165	0.1214 0.1302	3.04 3.05	3.04
76	0.4995 0.5115	0.3764 0.3852	0.5063 0.5200	0.1207 0.1235	3.25 3.26	3.26
71[1]		% 75.51 75.42 75.46		% 23.86 23.86 23.86		3.24
72[1]		75.49 75.37 75.43		23.70 23.80 23.75		3.26

[1] *Determinations made by P. E. Pelletier.*

TABLE XVIII*b*

Lead nitrate ($M/20$), arsenic oxide ($M/20$), and ammonium hydroxide ($M/20$ to M)

Precipitate No.	Conc. of solutions, moles per litre			Molar ratio NH_3/As_2O_5 in solutions	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors
	$Pb(NO_3)_2$ 4 litres	As_2O_5 2 litres	NH_4OH 2 litres			
74	0.05	0.05	0.05	1.0	1.98	1.5
70	0.05	0.05	0.15	3.0	2.02	2.0
69	0.05	0.05	0.25	5.0	3.04	6.7
76	0.05	0.05	0.35	7.0	3.26	9.0
71	0.05	0.05	0.50	10.0	3.24	9.4
72	0.05	0.05	1.00	20.0	3.26	9.9

FIGS. 14 and 15. FIG. 14. *Lead nitrate, arsenic oxide, and ammonium hydroxide.*
FIG. 15. *Influence of the pH on the composition of the precipitates.*

EFFECT OF HYDROGEN ION CONCENTRATION ON THE COMPOSITION OF THE LEAD ARSENATES

The pH values of the mother liquors were determined by means of the glass electrode. The results are shown in Table XIX and Fig. 15. The curve (Fig. 15), drawn from the data in this table, shows that, according to the hydrogen ion concentration, the precipitates obtained can be classified in three distinct groups: dilead arsenates in strongly acid solutions; slightly basic arsenates in neutral or slightly alkaline solutions; and strongly basic arsenates in strongly alkaline solutions.

TABLE XIX

INFLUENCE OF THE pH ON THE COMPOSITION OF THE LEAD ARSENATES

Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors	Molar ratio PbO/As_2O_5 in precipitates	pH values of the mother liquors
2.00	1.0	1.99	2.1	3.12	9.0
2.00	1.1	1.95	2.8	3.26	9.0
1.82	1.2	1.91	3.2	3.24	9.4
2.00	1.2	3.04	6.7	3.26	9.9
1.94	1.5	2.76	6.8	3.36	10.2
1.98	1.5	2.19	7.25	7.14	12.0
1.99	1.65	2.34	7.35	8.27	12.55
1.89	1.7	2.91	7.4	8.30	12.45
1.99	1.7	2.98	7.45	8.44	12.8
1.98	2.0	3.02	7.6	7.95	12.8
2.02	2.0	3.11	7.8	8.18	12.75

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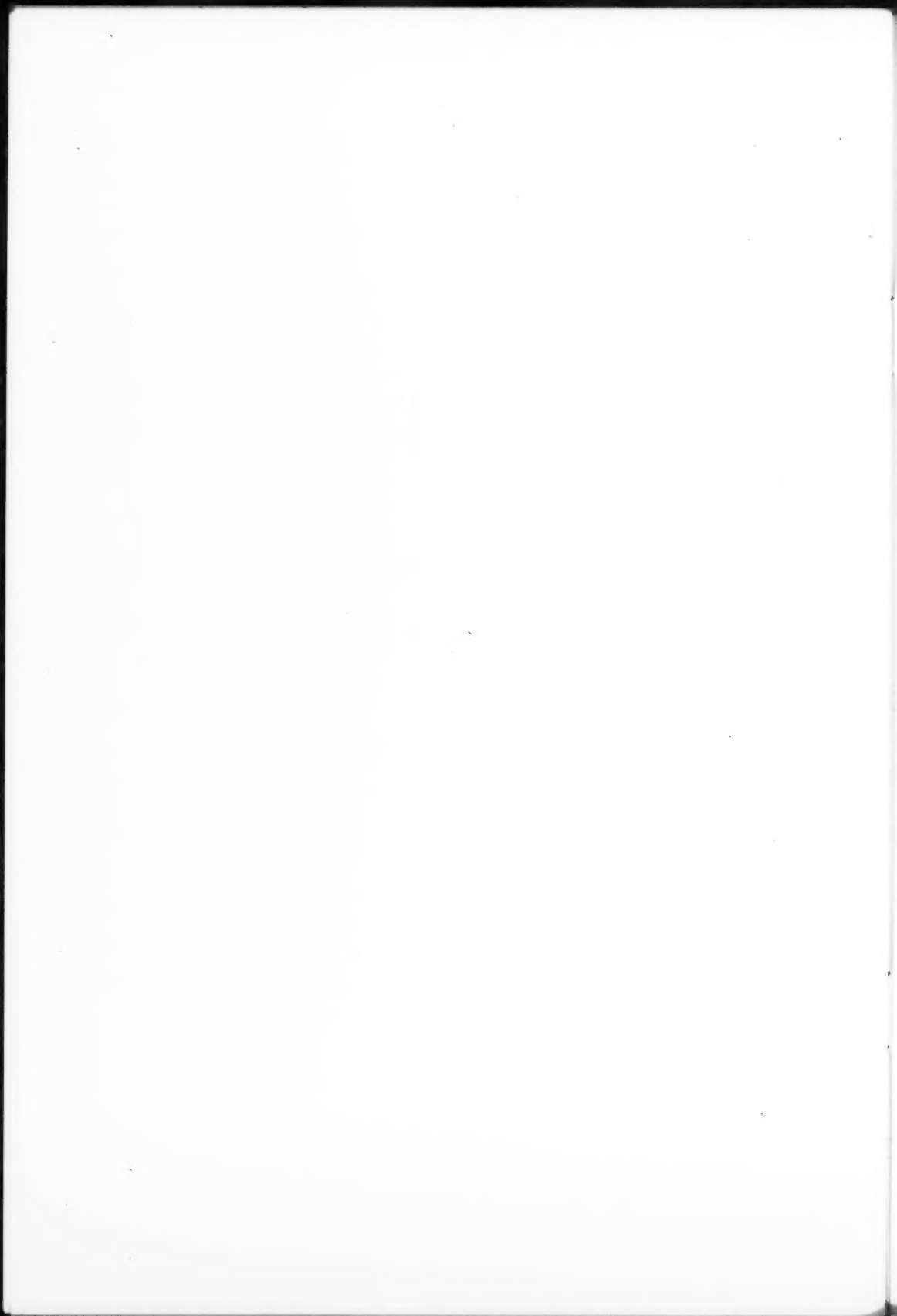
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